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ANTICORROSIVE AGENT AND CORROSION PROTECTION PROCESS FOR METAL SURFACES

This application is a continuation under 35 USC Sections 365(c) and 120 of International Application No. PCT/EP02/06888, filed 21 June 2002 and published 9 January 2003 as WO 03/002781, which claims priority from German Application No. 10131723.9, filed 30
5 June 2001, each of which is incorporated herein by reference in its entirety.

Background of the Invention

Field of the Invention

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This invention relates to the field of corrosion protection treatment of metal surfaces. One aspect of the invention involves depositing an anticorrosive layer onto the bare metal surface. A second aspect of the invention involves enhancing the
15 anticorrosive action of an anticorrosive layer already deposited onto the metal surface. A particular feature of the invention is that no toxic heavy metals, such as chromium or nickel, have to be used.

20 Discussion of the Related Art

There is extensive prior art relating to the deposition of anticorrosive layers onto bare metal surfaces and to the rinsing of already coated metal surfaces in order to increase corrosion
25 protection. Some examples of documents which deal in particular with the chromium-free treatment of aluminum surfaces are given below. The term "conversion treatment" used in this connection indicates that components of the treatment solution react chemically with the metal surface, resulting in the formation of

an anticorrosive layer into which both components of the treatment solution and metal atoms from the metal surface are incorporated.

5 The chromium-free conversion treatment of aluminum surfaces with fluorides of boron, silicon, titanium or zirconium, alone or in combination with organic polymers, in order to achieve a permanent corrosion protection and to produce a foundation for a subsequent coating is in principle known.

10 U.S. Pat. No. 5,129,967 discloses treatment baths for a no-rinse treatment (therein referred to as "dried in place conversion coating") of aluminum, containing:

- 15 a) 10 to 16 g/l polyacrylic acid or homopolymers thereof;
b) 12 to 19 g/l hexafluorozirconic acid;
c) 0.17 to 0.3 g/l hydrofluoric acid; and
d) up to 0.6 g/l hexafluorotitanic acid.

20 European Pat. No. 8942 discloses treatment solutions, preferably for aluminum cans, containing:

- a) 0.5 to 10 g/l polyacrylic acid or an ester thereof; and
b) 0.2 to 8 g/l of at least one of the compounds
25 H_2ZrF_6 , H_2TiF_6 and H_2SiF_6 , wherein the pH of the solution is below 3.5,

as well as an aqueous concentrate for replenishing the treatment solution, containing:

- 30 a) 25 to 100 g/l polyacrylic acid or an ester thereof;
b) 25 to 100 g/l of at least one of the compounds
 H_2ZrF_6 , H_2TiF_6 and H_2SiF_6 ; and
c) a source of free fluoride ions which provides 17 to
35 120 g/l free fluoride.

DE-C-1933013 discloses treatment baths having a pH of above 3.5 which, besides complex fluorides of boron, titanium or zirconium in quantities of 0.1 to 15 g/l, based on the metals, contain in addition 0.5 to 30 g/l oxidizing agent, in particular sodium metanitrobenzenesulfonate.

DE-C-2433704 describes treatment baths for increasing the coating adhesion and the permanent corrosion protection on, inter alia, aluminum; these baths may contain 0.1 to 5 g/l polyacrylic acid or salts or esters thereof, as well as 0.1 to 3.5 g/l ammonium fluoro-zirconate, calculated as ZrO_2 . The pH of these baths may vary over a wide range. The best results are generally obtained when the pH is from 6 to 8.

U.S. Pat. No. 4,992,116 describes treatment baths for the conversion treatment of aluminum having a pH of between about 2.5 and 5, which contain at least three components:

- a) phosphate ions within the concentration range of between 1.1×10^{-5} and 5.3×10^{-3} mol/l, corresponding to 1 to 500 mg/l,
- b) 1.1×10^{-5} to 1.3×10^{-3} mol/l of a fluorine acid of an element selected from Zr, Ti, Hf and Si (corresponding to 1.6 to 380 mg/l, depending on the element), and
- c) 0.26 to 20 g/l of a polyphenol compound, obtainable by the reaction of poly(vinylphenol) with aldehydes and organic amines.

Here, a molar ratio of fluorine acid to phosphate of about 2.5:1 up to 1:10 is to be maintained.

DE-A-2715292 discloses treatment baths for the chromium-free preliminary treatment of aluminum cans. These baths contain at least 10 ppm titanium and/or zirconium, between 10 and 1000 ppm phosphate and a quantity of fluoride sufficient for the formation of complex fluorides of the titanium and/or zirconium present, but at least 13 ppm, and have a pH of between 1.5 and 4.

WO 92/07973 discloses a chromium-free treatment process for aluminum which uses from 0.01 to about 18 wt.% H_2ZrF_6 and from 0.01 to about 10 wt.% of a 3-(N-C1-4-alkyl-N-2-hydroxyethylaminomethyl)-4-hydroxystyrene polymer as essential components in acidic aqueous solution. Optional components are 0.05 to 10 wt.% dispersed SiO_2 , 0.06 to 0.6 wt.% of a solubilizer for the polymer as well as a surfactant.

Notwithstanding this extensive prior art, of which only extracts are reported here, there is still a need for improved agents and processes for the corrosion protection treatment of metal surfaces.

The previously unpublished German Patent Application DE 10005113 is based on the finding that homo- or copolymers of vinylpyrrolidone have an excellent anticorrosive action. In a first aspect, that invention relates to a process for the corrosion protection treatment of a metal surface, which is characterized in that the metal surface is contacted with a homo- or copolymer of vinylpyrrolidone. Here, in a first embodiment of the invention, the metal surface may first of all be subjected to a conversion treatment according to prior art, for example, a phosphating using zinc or iron, a conversion treatment using fluoric acids of metals, for example, of titanium, zirconium or hafnium, or even of boron or silicon, or a treatment using a solution or suspension of an organic polymer which contains no vinylpyrrolidone units. Examples of such polymers are given in the literature cited in the introduction.

An alternative embodiment of the cited invention involves contacting the metal surface with a homo- or copolymer of vinylpyrrolidone at the same time that the metal surface is being subjected to a conversion treatment. In this case, the homo- or copolymer is therefore present in the treatment solution by means

of which a conversion layer is produced on the metal surface. The treatment solution for the production of the conversion layer may contain, for example, phosphoric acid or anions thereof. Divalent cations, such as zinc and/or manganese, may also be present in the treatment solution. A particular example of such a treatment solution for the production of a conversion layer is a zinc phosphating solution, which produces a crystalline layer of zinc-containing metal phosphates on the metal surface. The treatment solution may, however, also contain phosphoric acid and/or anions thereof, but no divalent metals. An example of this is an iron phosphating solution, which produces a substantially non-crystalline layer of metal phosphates and/or metal oxides on a metal surface, in particular an iron-containing surface. The presence of homo- or copolymers of vinylpyrrolidone in such a treatment solution improves the corrosion protection achieved by the conversion layer. This also applies if the treatment solution, in addition to homo- or copolymers of vinylpyrrolidone, contains fluoric acids and/or complex fluorides of metals and semi-metals, such as boron, silicon, titanium, zirconium and/or hafnium, as components forming the conversion layer.

According to DE 10005113 cited above, the ready-to-use solution for treating metal surfaces preferably contains between 0.05 and 200 g/l of a homo- or copolymer of vinylpyrrolidone. The set object of the present invention is to improve on the subject matter of DE 100 05 113 with regard to the efficiency of the chemicals used.

Brief Summary of the Invention

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The present invention relates to an agent for treating metal surfaces, which contains phosphoric acid and/or at least one fluoric acid of one or more elements selected from Zr, Ti, Hf and Si or the respective anions thereof, as well as a homo- or copolymer of vinylpyrrolidone, characterized in that it is in the form of a ready-to-use solution for application, containing

- a) 0.02 to 20 g/l phosphoric acid and/or at least one fluorine acid of one or more elements selected from Zr, Ti, Hf and Si or the respective anions thereof, as well as
b) 10 to 49.9 mg/l of a homo- or copolymer of vinylpyrrolidone.

5

Detailed Description of Certain Embodiments of the Invention

Where phosphoric acid is present, the agent for treating metal surfaces is a phosphating solution. If this does not contain ions of divalent metals, such as zinc and/or manganese, it is a so-called "non-layer-forming" phosphating solution, for example, it may be in the form of an iron phosphating solution. Phosphating solutions containing zinc and/or manganese, which contain, for example, 0.3 to 2 g/l zinc ions and, if desired, in addition to or instead of this about the same concentration of manganese ions, are referred to as so-called "layer-forming" phosphating solutions in the field of conversion treatment. The treatment solution may also contain one or more fluorine acids of one or more elements selected from Zr, Ti, Hf and Si, together with or instead of phosphoric acid. Depending on the adjusted pH of the solution, both phosphoric acid and the above-mentioned fluorine acids are present partly in the form of singly or multiply negatively charged anions. The ratio of acidic anions to undissociated acid depends on the protolysis constant of the respective acid and on the pH actually established. This phenomenon is generally known as the acid-base equilibrium. In addition to the above-mentioned essential components, the agents contain water and, if desired, other active components or auxiliary substances in order to adjust the pH, increase the anticorrosive action, improve the ease of application and possibly for other purposes.

If the agents according to the invention contain copolymers of vinylpyrrolidone, these copolymers may contain one or more other monomers in addition to vinylpyrrolidone. They may therefore be, for example, copolymers comprising 2 components or copolymers

comprising 3 components(= terpolymers). Mixtures of homopolymers and two-component copolymers, of homopolymers and terpolymers or of two-component polymers and terpolymers, may also be used.

5 The ready-to-use agent can be obtained by diluting a concentrate; this is the subject matter of the previously unpublished German Patent Application DE 100 05 113. Depending on the specific composition, it may be that concentrates which already contain all the active components are not sufficiently stable in storage
10 for long periods. In these cases, it is preferable to divide the concentrates up into at least two components, each containing selected components of the ready-to-use anticorrosive agent. For example, it may be advisable that one component of the concentrate contain at least predominantly the inorganic
15 constituents of the agent, while at least one other component of the concentrate contains the organic polymers. The two components of the concentrate may then have different pH values, thus enabling the stability of the concentrate components in storage to be enhanced. In order to prepare or to replenish the agent in
20 its ready-to-use form, the individual components of the concentrate are diluted with water to the extent that the active components are present in the required concentration range. Here, it may be necessary to adjust the pH to within the required range by adding an acid or a lye.

25 Preferred concentration ranges for the active components a) and b) in the solution for application, in the case of phosphoric acid or phosphate ions, are 5 to 20 g/l, in particular 8 to 16 g/l phosphate ions, and in the case of the fluoric acids are a
30 quantity such that Zr, Ti, Hf and/or Si, based on these elements, are present in a concentration within the range of between 20 and 1000 mg/l, in particular 50 to 400 mg/l. The concentration of the homo- or copolymers of vinylpyrrolidone in the solution for application is preferably within the range of 20 to 45 mg/l.

35

Suitable homo- or copolymers of vinylpyrrolidone are, for example, the polymers listed in Table 1 or polymers of the monomers named therein.

5 Table 1: Examples of homo- or copolymers of vinylpyrrolidone

Name	Trade Name and Manufacturer
Vinylpyrrolidone, homopolymer	Luviskol [®] , BASF/ ISP
Vinylpyrrolidone/Vinyl acetate	Luviskol [®] , BASF/ ISP
Vinylpyrrolidone/Vinylcaprolactam	Luvitec [®] , BASF
Vinylpyrrolidone/Vinylimidazole	Luvitec [®] , BASF
Vinylpyrrolidone/Vinylimidazolium methyl sulfate	Luvitec [®] , BASF
Vinylpyrrolidone/Na methacrylate	Luvitec [®] , BASF
Vinylpyrrolidone/olefins	ISP [®] , Antaron
Vinylpyrrolidone/Dimethylaminoethyl methacrylate	ISP [®]
Vinylpyrrolidone/Dimethylaminopropyl-methacrylamide	ISP [®] , Styleze
Vinylpyrrolidone/Dimethylaminoethyl methacrylate, ammonium salt	ISP [®] , Gafquat
Vinylpyrrolidone/Vinylcaprolactam/Dimethyl-aminoethyl methacrylate	ISP [®]
Vinylpyrrolidone/Methacrylamidopropyltrimethyl ammonium chloride	ISP [®] , Gafquat
Vinylpyrrolidone/Vinylcaprolactam/Dimethyl-aminoethyl methacrylate	ISP [®] , Advantage
Vinylpyrrolidone/Styrene	ISP [®] , Antara

10 In order to increase the corrosion protection, the agents according to the invention may contain other transition metal

ions, such as ions of the elements zinc, manganese, cerium or vanadium, also hydrofluoric acid or free fluorides. The presence of chromium ions or nickel ions may in principle also have advantages. However, for reasons of industrial safety and environmental protection, the addition of chromium ions or nickel ions is preferably avoided. Consequently, in a preferred embodiment of the invention, the agent is free from nickel and chromium. This means that these metals or compounds thereof are not intentionally added to the agent. The possibility cannot be ruled out, however, that ions of nickel and/or chromium, originating from the material of the tank or from the surfaces to be treated, such as steel alloys, will enter the agent (the treatment solution) in low concentrations. However, in practice, it is anticipated that the concentrations of nickel and/or chromium in the ready-to-use treatment solution will not be more than about 10 ppm.

The ready-to-use agent according to the invention has a pH preferably in the range of 1 to 6 and in particular in the range of 2 to 5.5. This means that the fluoric acids of the elements Zr, Ti, Hf or Si, depending on pH and protolysis constants, are partly in the form of the free acids, but partly in the form of the acidic anions thereof. It is therefore irrelevant whether these fluoric acids are used as such or in the form of the salts. Furthermore, acid-soluble compounds of Zr, Ti, Hf or Si, as well as hydrofluoric acid or soluble fluorides may be added separately, as the fluoro anions of the above-mentioned elements can be formed from these. Depending on the method of use, the pH has to be adjusted to the desired range by addition of acid, such as the free fluoric acids of the above-mentioned elements, but even, for example, hydrofluoric acid, sulfuric acid, nitric acid or phosphoric acid or by addition of a base, such as alkali metal carbonate solution, alkali metal hydroxide solution or ammonia.

By reason of the especially good anticorrosive action of homo- or copolymers of vinylpyrrolidone which contain caprolactam groups,

in a particular embodiment the agent according to the invention contains homo- or copolymers of vinylpyrrolidone containing caprolactam groups.

5 A further aspect of the invention is a process for treating metal surfaces, wherein the metal surfaces which, if desired, may already carry an anticorrosive layer, are contacted with the above-mentioned agent. The metal surfaces may be selected, for example, from surfaces made of steel, zinc-plated steel
10 (electroplated or hot-dip galvanized), steel coated with zinc alloy, or of aluminum or magnesium. Here, the metals aluminum and magnesium are generally not in pure form, but in the form of alloys with other elements, such as lithium, zinc, copper, silicon, magnesium (in the case of aluminum alloys) or aluminum
15 (in the case of magnesium alloys). The process is envisaged in particular for the treatment of surfaces made of those metals which are used in the construction of vehicles, in the household appliance industry, or in the field of architecture or furnishings.

20 In this connection, those metal surfaces which as yet have no anticorrosive layer may be treated. The treatment process according to the invention then produces an anticorrosive coating, which at the same time improves the adhesion of an
25 organic coating, such as a lacquer, optionally to be applied subsequently. However, those metal surfaces which already have a previously formed anticorrosive layer may also be treated by the process according to the invention. In this case, the anticorrosive action of this previously applied anticorrosive
30 layer is further improved. For example, the process according to the invention is suitable for the aftertreatment of metal surfaces which have an X-ray-amorphous or crystalline coating, such as are produced, for example, by a non-layer-forming or a layer-forming phosphating, for instance, a layer-forming zinc
35 phosphating. The treatment according to the invention of such pretreated metal surfaces results in the closure of the pores

remaining in the initial anticorrosive layer after the pretreatment.

5 In the treatment process according to the invention, the metal surfaces may be contacted with the treatment solution, for example, by spraying or dipping. In this case, it is preferable to arrange that the treatment solution be rinsed off with water after a contact time, which may range, for example, from 30 seconds to 5 minutes. Alternatively, the treatment solution may
10 be contacted with the metal surface in the so-called no-rinse process. Here, the treatment solution is either sprayed onto the metal surface or transferred onto the surface by spreading rollers. After a contact time, which may range, for example, from 2 to 20 seconds, the treatment solution is then dried without
15 further intermediate rinsing. This may take place, for example, in a heated furnace.

For the treatment process according to the invention, the treatment solution has a pH preferably in the range of 1 to 6.
20 However, narrower pH ranges may be preferred, depending on the substrate and method of application and the contact time. For example, the pH is adjusted preferably to within the range of 2 to 6 for the treatment of bare metal surfaces; in particular to within the range of 2 to 4 for the treatment of aluminum surfaces
25 and in particular to within the range of 3 to 5 for the treatment of steel, zinc or zinc-plated steel. Already pretreated metal surfaces having, for example, a phosphate layer, are preferably contacted with a treatment solution having a pH in the range of 3.5 to 5. The temperature of the treatment solution in the course
30 of the process according to the invention may generally be between the freezing point and the boiling point of the treatment solution, temperatures in the region of room temperature or above being preferred for practical reasons. For example, the temperature of the treatment solution may be within the range of
35 15 degrees C to 60 degrees C and in particular from 20 degrees C to 45 degrees C.

The treatment process according to the invention is one step in an otherwise conventional sequence of steps in the field concerned. For example, the metal surfaces to be treated are usually cleaned using a conventional cleaning solution prior to the treatment according to the invention. However, the cleaning step may be omitted if, immediately before the treatment according to the invention, the metal surfaces to be treated are coated, for example, zinc-plated, or are subjected to a conversion treatment, for example, a phosphating. After the treatment step according to the invention, the metal surfaces are conventionally coated with an organic coating, for instance, a lacquer. This may be a powder coating, for example, or an electrolytically, especially cathodically, precipitable electrophoretic coating.

A particularly preferred procedure in carrying out the process according to the invention involves treating the metal surface with an aqueous solution of an acid prior to its being contacted with the above-mentioned agent in order to produce a conversion layer, i.e., during a conversion treatment. The inserted processing step, involving the treatment of the metal surface with an aqueous solution of an acid prior to the conversion treatment, is also referred to in the industry as "acid pickling" or "pickle passivation". Acids which are conventionally used for acid pickling or pickle passivation can be employed for this purpose in the procedure according to the invention. An example of these is phosphoric acid.

Examples: Use as a conversion treatment

Example 1: Conversion process with previous pickle passivation

Substrates: Hot-dip galvanized steel (HDG), electrolytically galvanized steel (EG), aluminum (AC120), cold-rolled steel (CRS)

Order of procedure (spray application):

5

1. Cleaning:	Ridoline® 1570, 3%; 82 seconds, 55 degrees C Ridosol® 1270, 0.3% (commercial metal cleaner manufactured by Henkel KGaA)
2. Rinse:	deionized water
3. Pickle passivation:	phosphoric acid, 0.23%, 82 seconds
4. Rinse:	deionized water
5. Conversion treatment:	108 seconds; 30 degrees C, using an aqueous solution containing H ₂ ZrF ₆ acid (45%; 1.38 g/l) and vinylpyrrolidone/vinylcaprolactam polymer (37 mg/l solids content)
6. Rinse:	deionized water
7. Drying:	compressed air
8. Coating:	lead-free cathodic electrophoretic coating (BASF CG 310)
Thickness of coating:	20-23 µm

Example 2: Order of procedure as above, but without steps 3 and

10 4

Corrosion test:

Galvanized

substrates: Coating adhesion after storage in salt water

Aluminum: Copper-accelerated salt spray test CASS

DIN 50021, 10 days

Steel: Salt spray test SS DIN 50021, 21 days

Results: Creepage along scribe (half scribe width):

U/2 in mm; Results of the stone-impact test for coating adhesion

(K value, K = 1: best coating adhesion, K = 10: worst coating adhesion)

	CRS	HDG	EG	AC120
Example				
	U/2 mm	K	K	U/2 mm
With step 3, 4	0.7	8	9	0.8
Without step 3, 4	1.6	10	10	0.9

Example 3: Conversion process with subsequent powder coating (galvanized steel) using copolymer mixtures

Substrates: CRS, EG, HDG

Order of procedure (dipping application):

1. Cleaning:	Ridoline® 1570, 2%; Ridosol® 1237, 0.3%; 5 minutes; 55 degrees C (commercial metal cleaner manufactured by Henkel KGaA)
2. Rinse	deionized water
3. Conversion treatment:	180 seconds; 30 degrees C, using one of the following bath formulations: H ₂ ZrF ₆ acid (45%; 1.38 g/l) + vinylpyrrolidone/vinylcaprolactam copolymer (= P _a) + vinylpyrrolidone/vinylimidazole copolymer (= P _b) (37 mg/l solids content)
4. Rinse:	deionized water
5. Drying:	compressed air
6. Coating:	Polyester PES 5807/RAL 5009 GL (TIGC-free, product of the firm of Herbert); approx. 60-80 µm

5

Corrosion test

Neutral salt spray test DIN 50021 SS, 21 days

- 10 Results: Creepage of paint along scribe, half scribe width; coating adhesion by the cross-cut adhesion test

Example	Creepage	Cross-cut (scale 0 to 5)
CRS	1.7 mm	0
EG	2.5 mm	0
HDG	1.8 mm	0

The proportions of polymers can be varied, for example between homo- and/or copolymers $P_a\% = 100\% - P_b\%$, with $P_a > 0$.

Example 4: Conversion process using copolymer mixtures (powder coating)

Substrate: CRS

Order of procedure (dipping application):

1. Cleaning:	Ridoline® 1570, 2%; Ridosol® 1237, 0.3%; 5 minutes; 55 degrees C
2. Rinse:	deionized water
3. Conversion Treatment:	180 s; 30 degrees C, using one of the bath formulations according to the Table below <div style="text-align: right; margin-right: 100px;">H_2ZrF_6 acid</div> (45%; 1.38 g/l) + vinylpyrrolidone/vinylcaprolactam copolymer ($= P_b$) + vinylpyrrolidone/vinylimidazole copolymer ($= P_a$) (22 mg/l solids content)
4. Rinse:	deionized water
5. Drying:	compressed air
6. Coating:	Polyester PES 5807/RAL 5009 GL (TIGC-free, product of the firm of Herbert); approx. 60-80 μm

Corrosion test

Neutral salt spray test DIN 50021 SS, 21 days

Polymer	Creepage
100% P_a	3.9 mm
70% P_a	2.3 mm